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(54) Title: LOW RESIDUE HAIR CARE COMPOSITIONS USING GRAFTED COPOLYMERS		
(57) Abstract The present invention relates to rinse-off hair care compositions which provide styling and hair conditioning properties without the formation of a non-removable residue. The compositions comprise from about 0,25 % to about 70 % of a copolymer component comprising from about 1.5 % to about 70 % of a silicone-grafted adhesive hair styling copolymer having a weight average molecular weight from about 300,000 to about 5,000,000 and from about 30 % to about 98.5 % of a hydrophobic volatile solvent.		

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LOW RESIDUE HAIR CARE COMPOSITIONS USING GRAFTED COPOLYMERS

TECHNICAL FIELD

The present invention relates to rinse-off hair care compositions containing a hydrophobic silicone grafted copolymer and a hydrophobic, volatile solvent for the copolymer, which deliver the combined conditioning and style retention properties typical of these copolymers without the formation of a non-removable residue on hair shafts. Examples of hair care composition to which this invention relates are hair conditioners, hair styling rinses, rinse-off hair styling mousse and gels, and shampoos useful for cleansing, styling and conditioning the hair.

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration can be accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays after washing and conditioning the hair. This approach presents several significant drawbacks to the user. It requires a step, in addition to shampooing and/or conditioning, to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application.

Recently, it has become known to utilize hydrophobic silicone grafted organic backbone copolymers as hair setting agents in rinse-off hair styling/conditioning compositions (e.g., shampoos, rinses, mousses, gels and conditioners). Compositions containing these copolymers provide the combined style retention and conditioning and/or cleansing benefits, without an application step in addition to shampooing/conditioning. These rinse-off styling/conditioning compositions typically comprise a hydrophobic, silicone grafted copolymer solubilized in a suitable hydrophobic, volatile solvent. The hydrophobic copolymer/solvent component deposits on the hair when applied during washing, conditioning or rinsing, but is not readily removed during the final rinsing with water. As the hair is dried, during or after styling, the volatile solvent evaporates to leave hair treated with the styling/conditioning copolymer.

A hair styling/conditioning copolymer should provide certain styling and conditioning benefits. The copolymer should have sufficient adhesive strength to remain on the hair after application. The copolymer should have cohesive strength and elasticity properties to provide the ability to style the hair, with or

without heated implements, and then to maintain the new hair style. The copolymer should leave hair feeling soft, not as stiff as conventional resins. Such a hair styling copolymer needs to be easily cleaned from the hair (i.e., by shampooing) to prevent a build-up of the copolymer.

Hair care compositions containing various copolymer are well-known in the prior art. However, none of these references either teach or suggest compositions having a low visible residue on the hair. See for example, U.S. Patent No. 3,208,911, to Oppliger, issued September 28, 1965, U.S. Patent No. 4,601,902, to Fridd et al, issued July 22, 1986, U.S. Patent No. 4,654, 161, to Kollmeier et al., issued March 31, 1987, U.S. Patent No. 5,106,609, to Bolich hr. et al., issued April 21, 1992, U.S. Patent No. 4,693,935, to Mazurek, issued September 15, 1987, European Patent Application No. 412,704, to Bolich et al., published February 2, 1991

It has been observed, however, that hydrophobic, silicone grafted copolymers may be more difficult to remove from the hair by shampooing, than typical hair styling resins and gums. It is often observed, that after repeated cycles of gentle shampooing and towel/air drying, residual styling copolymer can build up on the hair to a point where the residue completely surrounds the hair shaft. At this point the residue cannot be removed from the hair with normal shampooing. This build-up results in severe cosmetic and combability problems for the user of these hair care products. Without being limited by theory, it is believed that the adhesive strength of the copolymer to the hair is too high relative to the internal cohesive breaking strength. This results in a situation, during gentle washing, in which styling copolymer films fracture and are removed in pieces. Some pieces remain adhered to the hair shaft and are coated with new copolymer during the next application of the composition. The residual pieces act as sites for the formation of the build-up of copolymer.

It has now been found that rinse-off compositions utilizing specifically defined hydrophobic, silicone grafted adhesive hair styling copolymers provide excellent hair conditioning and hair styling properties, and yet are easily removed from the hair by shampooing.

It is an object of the present invention to formulate rinse-off hair care compositions which provide effective hair conditioning and/or cleansing and style retention properties, in which the conditioning and styling copolymer can be easily removed from the hair by shampooing.

It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention in one product, in which the conditioning and styling copolymer can be easily removed from the hair by shampooing.

It is a further object of the present invention to provide an improved method for styling and conditioning hair by utilizing a single rinse-off hair care composition.

These and other objects, as may be apparent from the description below, can be obtained by the present invention.

The present rinse-off hair care compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based on total composition unless otherwise indicated.

All ingredient levels refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

SUMMARY OF THE INVENTION

The present invention relates to a rinse-off hair care composition comprising:

- A. from about 0.25% to about 70% of a copolymer component comprising:
 - i. from about 1.5% to about 70%, by weight of said copolymer component, of a silicone-grafted adhesive hair styling copolymer having a weight average molecular weight from about 300,000 to about 5,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising monomers selected from the group consisting of A monomers, B monomers, C monomers and mixtures thereof;

wherein the weight percent of said copolymer in said rinse-off hair care composition is from about 0.10% to about 7%; and

wherein said copolymer is prepared by the polymerization combination of the following relative weight percentages of said A monomers, said B monomers, and said C monomers:

 - a. from about 45% to about 85% of a hydrophobic, vinyl A monomer, free radically copolymerizable with said B monomers and said C monomers;
 - b. from 0% to about 5% of a hydrophilic, reinforcing B monomer, copolymerizable with said A monomers and said C monomers, said B monomer being selected from the group consisting of polar monomers and macromers and mixtures thereof; and
 - c. from about 15% to about 50% of a polysiloxane-containing C monomer, copolymerizable with said A monomers and said B monomers, having:

a weight average molecular weight of from about 5,000 to about 50,000; and

having the general formula:

$$X(Y)_nSi(R)_{3-m}(Z)_m$$

wherein:

X is a vinyl group copolymerizable with said A monomers and said B monomers;

Y is a divalent linking group;

R is a hydrogen, lower alkyl, aryl or alkoxy;

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

m is an integer from 1 to 3; and

- ii. from about 30% to about 98.5% by weight of said copolymer component, of a hydrophobic volatile solvent; and
- B. from about 30% to about 99.75% of a carrier suitable for application to hair; and wherein said rinse-off hair care composition has a residue index on hair of greater than about 20.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

The hydrophobic copolymers of the present invention can be described as graft copolymers. The term "graft copolymers" is familiar to one of ordinary skill in polymer science and is used herein to describe the copolymers which result by adding or "grafting" a polymeric chemical moiety (i.e. "grafts") onto another polymeric moiety commonly referred to as the "backbone". The backbone typically has a higher molecular weight than the grafts. Thus, graft copolymers can be described as polymers having pendant polymeric side chains, and as being formed from the "grafting" or incorporation of polymeric side chains onto or into a polymer. The polymer to which the grafts are incorporated can be homopolymers or copolymers, e.g. linear random or block polymers. Such polymers are derived from a variety of monomer units.

The term "hydrophobic" is used herein consistent with its standard meaning of lacking affinity for water, whereas "hydrophilic" is used herein consistent with its standard meaning of having affinity for water. As used herein in relation to monomer units and polymeric materials, including the copolymers, and solvents for the copolymers, "hydrophobic" means substantially water insoluble; "hydrophilic" means substantially water soluble. In this regard, "substantially water insoluble" shall refer to a material that is not soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and preferably not soluble at 0.1% by weight (calculated on a water plus monomer or polymer weight basis). "Substantially water soluble" shall refer to a material that is soluble in distilled (or equivalent) water, at 25°C, at a concentration of 0.2% by weight, and are preferably soluble at 1.0% by weight. The terms "soluble", "solubility" and the like, for purposes hereof, corresponds to the maximum concentration of

monomer or polymer, as applicable, that can dissolve in water or other solvents to form a homogeneous solution, as is well understood to those skilled in the art.

The term "rinse-off", as contrasted with the term "leave-on", is used herein to mean that the compositions of the present invention are used in a context whereby the composition is ultimately rinsed or washed from the hair either after or during the application of the product. A "leave-on" product, refers to a hair care composition that is applied to the hair and not further subjected to a rinsing step. Nonlimiting examples of rinse-off products of the present invention include hair conditioners, hair styling rinses, rinse-off hair styling mousse and gels, and shampoos.

The term "suitable for application to human hair" as used herein, means that the compositions or components thereof so described are suitable for use in contact with human hair and the scalp and skin without undue toxicity, incompatibility, instability, allergic response, and the like.

The aforementioned definitions shall also apply to other materials so described herein, to the extent any other definitions regarding such materials are consistent with those stated above.

The compositions of the present invention comprise the following essential components.

Copolymer Component

The rinse-off compositions of the present invention comprise, from about 0.25% to about 70%, preferably from about 4% to about 30%, and more preferably from about 8% to about 18%, by weight of the composition, of a copolymer component. The copolymer component comprises a silicone grafted adhesive hair styling copolymer and a suitable hydrophobic volatile solvent. It is not intended to exclude the use of higher or lower levels of the copolymers, as long as an effective amount is used to provide hair styling and hair conditioning properties to the composition and the composition can be formulated and effectively applied for its intended purpose.

Silicone Grafted Adhesive Hair Styling Copolymer

The copolymer component of the compositions of the present invention comprises from about 1.5% to about 70%, preferably from about 5.0% to about 40%, more preferably from about 10% to about 25%, by weight of the copolymer component, of a silicone grafted adhesive copolymer. The overall rinse-off hair care composition comprises from about 0.10% to about 7.0%, preferably from about 1.0% to about 4.0%, more preferably from about 1.5% to about 2.5% of the silicone grafted adhesive copolymer. It is not intended to exclude the use of higher or lower levels of the copolymers, as long as an effective amount is used to provide adhesive and film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By "adhesive" it is meant that when applied as a solution to a surface and dried, the copolymer forms a film which attaches to the surface. Such a film will have adhesive strength, cohesive breaking strength, and cohesive breaking strain.

The silicone grafted adhesive copolymers of the copolymer component of the present invention comprise an organic backbone preferably a carbon backbone derived from ethylenically unsaturated

monomers, such as a vinyl polymeric backbone, and a polysiloxane macromer grafted to the backbone. These copolymers are comprised of non-silicone containing, hydrophobic, free radically polymerizable vinyl "A" monomers, copolymerizable with the "B" and/or "C" monomers; grafted polysiloxane-containing vinyl "C" monomers, copolymerizable with "A" and "B" monomers; and, optionally, non-silicone containing, hydrophilic reinforcing "B" monomers which are polymerizable with the "A" and/or "C" monomers.

The silicone grafted copolymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone. The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers to which polysiloxane moieties are pendant. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri, or tetra-substituted. The backbone can also include ether groups, ester groups, amide groups, urethane groups and the like. The polysiloxane moieties can be grafted onto a copolymer backbone or the copolymer can be made by copolymerization of polysiloxane-containing polymerizable monomers at the chain end (e.g., ethylenically unsaturated monomers) with non-polysiloxane-containing copolymerizable monomers. The term "copolymerizable" is used herein to describe a material which can be reacted with another material (e.g. the A monomers, B monomers and C monomers of the present invention) in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. The preferred copolymerization synthetic technique is free radical polymerization.

The silicone grafted adhesive hair styling copolymer can have a weight average molecular weight of from about 300,000 to about 5,000,000, preferably from about 500,000 to about 2,000,000, more preferably from about 600,000 to about 1,500,000.

Preferably, the adhesive copolymer hereof, when dried to form a film will have a T_g or T_m of at least about -20°C, more preferably at least about 25°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "T_g" refers to the glass transition temperature of the backbone of the polymer, and the abbreviation "T_m" refers to the crystalline melting point of the backbone, if such a transition exists for a given polymer.

The silicone grafted copolymers of the compositions of the present invention comprise "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone graft pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

The silicone grafted copolymers should satisfy the following three criteria:

- (1) when dried the copolymer phase-separates into a discontinuous phase which includes the polysiloxane portion and a continuous phase which includes the non-polysiloxane portion;
- (2) the polysiloxane portion is covalently bonded to the non-polysiloxane portion; and

- (3) the number average molecular weight of the polysiloxane-containing C monomer is from about 5,000 to about 50,000.

When used in a composition, such as a rinse-off hair care composition, the non-polysiloxane portion should permit the copolymer to deposit on the hair.

Without being limited by theory, it is believed that the phase separation property provides a specific orientation of the copolymer which results in the desired combination of tactile feel, film-forming or adhesive benefits, and the ability to dry quickly and completely. The phase-separating nature of the compositions of the present invention may be determined as follows.

The copolymer is cast as a solid film out of a solvent (i.e., a solvent which dissolves both the backbone and the polysiloxane-graft portions). This film is then sectioned and examined by transmission electron microscopy. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein, said thesis incorporated by reference herein in its entirety).

A second method for determining phase-separating characteristics when silicone containing copolymers are used involves examining the enrichment of the concentration of silicone at the surface of a copolymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the copolymer surface. This produces a surface with the silicone oriented at the surface of the film. This can be demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone copolymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

The copolymers of the present invention are prepared by the polymerization combination of A monomers, C monomers and, if used, B monomers. The silicone grafted copolymers can be synthesized by free radical polymerization of the polysiloxane-containing monomers with the non-polysiloxane-containing monomers. The general principles of free radical polymerization methods are well understood. See, for example, Odian, "Principles of Polymerization", 3rd edition, John Wiley & Sons, 1991, pp. 198-334, incorporated by reference herein. The desired A, B, and C monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used.

Alternatively, redox or radiation initiation can be used. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the copolymer by addition of a nonsolvent. The copolymer can be further purified, as desired.

As an alternative to a batch reaction, the copolymer can be made by a semi-continuous or continuous process. In the semi-continuous process, two or more additions of monomers are made during the polymerization reaction. This is advantageous when the copolymer is made of several monomers which react during the polymerization at different rates. The proportions of monomers added to the reaction at the separate points of addition can be adjusted by one of ordinary skill in the art such that the polymers of the final product have a more uniform structure. In other words, the polymers of the final product will have a more consistent monomer content distribution for each of the monomer types charged to the reaction.

Examples of related copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. Additional silicone grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein in their entirety.

The particular relative amounts of A monomers, B monomers, and C monomers can vary as long as the copolymer backbone is soluble in the hydrophobic, volatile solvent hereof and the silicone grafted copolymer exhibits phase separation when dried.

The copolymers are prepared by the polymerization combination of A monomer, C monomer and, if used, B monomer. The copolymer composition is characterized by the amount of each monomer charged to the polymerization reaction vessel. In general, the silicone grafted, adhesive hair styling copolymer will comprise from about 45% to about 85%, preferably from about 60% to about 85%, more preferably from about 70% to about 80%, most preferably from about 70% to about 75% of the hydrophobic, vinyl A monomer; from 0% to about 5.0%, preferably from 0% to about 3.0% of the hydrophilic, reinforcing B monomer; and from about 15% to about 50%, preferably from about 15% to about 40%, more preferably from about 20% to about 30% of the polysiloxane-containing C monomer. The combination of the A monomers and B monomers preferably comprises from about 50.0% to about 85%, more preferably about 60% to about 85%, most preferably from about 70% to about 80% of the copolymer.

The hydrophobic vinyl A monomer, which is free radically copolymerizable with B monomers and C monomers, is selected from the group consisting of acrylic acid esters, methacrylic acid esters, vinyl compounds, vinylidene compounds, unsaturated hydrocarbons, C_1 - C_{18} alcohol esters of organic acids and organic acid anhydrides, and mixtures thereof. Representative examples of hydrophobic vinyl A monomers are acrylic or methacrylic acid esters of C_1 - C_{18} alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; styrene; polystyrene monomer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include t-butyl acrylate, t-butyl methacrylate, t-butyl styrene, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate; and mixtures thereof. Most preferably, A is selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, and mixtures thereof.

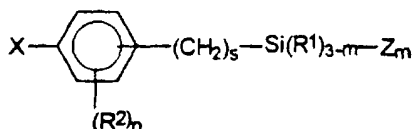
The hydrophilic, reinforcing B monomer, which is copolymerizable with the A and C monomers, is selected from the group consisting of unsaturated organic mono- and poly- carboxylic acids, unsaturated (meth)acrylates, unsaturated (meth)acrylamides, unsaturated (meth)acrylate alcohols, unsaturated aminoalkylacrylates, unsaturated organic acid anhydrides, unsaturated esters of organic acid anhydrides, hydrophilic unsaturated vinyl compounds, hydrophilic unsaturated allyl compounds, hydrophilic unsaturated imides, salts of the foregoing compounds, and mixtures thereof. Representative examples of hydrophilic reinforcing B monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), salts of any acids and amines listed above, and mixtures thereof. Preferred B monomers include monomers selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, methacrylamide, N t-butyl arylamide, dimethylaminoethyl methacrylate, t-butyl acrylamide, vinyl pyrrolidone, salts thereof and alkyl quaternized derivatives thereof, and mixtures thereof.

The polysiloxane-containing C monomer, copolymerizable with the A and B monomers, is exemplified by the general formula:

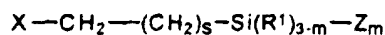


wherein X is an ethylenically unsaturated group copolymerizable with the A and B monomers, such as a vinyl group; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. The C monomer has a weight average molecular weight from about 5000 to about 50,000, preferably from about 5,000 to about 30,000, more preferably from about 8,000 to about 25,000.

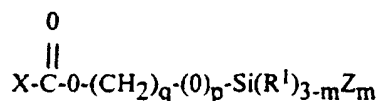
Preferably, the C monomer has a formula selected from the following formulas:



or



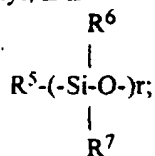
or



In these structures s is an integer from 0 to about 6, preferably 0, 1, or 2, more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; R² is C₁-C₁₀ alkyl or C₇-C₁₀ alkylaryl, preferably C₁-C₆ alkyl or C₁-C₁₀ alkylaryl, more preferably C₁-C₂ alkyl; n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl, preferably R¹ is alkyl; X is



R³ is hydrogen or -COOH, preferably R³ is hydrogen; R⁴ is hydrogen, methyl or -CH₂COOH, preferably R⁴ is methyl; Z is



R⁵, R⁶, and R⁷, independently are lower alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen or hydroxyl, preferably R⁵, R⁶, and R⁷ are alkyls; and r is an integer of from about 60 to about 700, preferably about 60 to about 400, more preferably r is from about 100 to about 350. Most preferably, R⁵, R⁶, and R⁷ are methyl, p=0, and q=3.

When the C monomer molecular weight is less than or equal to about 13,000, preferably from about 8,000 to about 13,000, and r is less than or equal to about 170, preferably from about 100 to about 170, the weight percentage of the C monomer charged to the polymerization process is preferably from about 25% to about 40%, more preferably 25% to about 30%. When the C monomer molecular weight is greater than about 13,000, preferably from about 13,000 to about 50,000, and r is greater than 170 or greater, preferably from about 170 to about 350, the weight percentage of the C monomer charged is preferably from about 20% to about 50%, more preferably 20% to about 30%.

Exemplary silicone grafted polymers for use in the present invention include the following, where the composition of the copolymer is given as weight percentage of each monomer used in the polymerization reaction used to prepare the copolymer.

- (i) 900,000 molecular weight copolymer of 75%/25% charged
t-butyl acrylate/polydimethylsiloxane molecular weight about 11,000
- (ii) 900,000 molecular weight copolymer of 80%/20% charged
t-butyl acrylate/polydimethylsiloxane molecular weight about 15,000
- (iii) 300,000 molecular weight copolymer of 70%/30% charged
t-butyl styrene/polydimethylsiloxane molecular weight about 20,000
- (iv) 700,000 molecular weight copolymer of 67%/3%/30% charged
t-butyl acrylate/acrylic acid/polydimethylsiloxane molecular weight about 11,000
- (v) 1,000,000 molecular weight copolymer of 65%/35% charged
t-butyl acrylate/polydimethylsiloxane molecular weight about 30,000
- (vi) 700,000 molecular weight copolymer of 70%/5%/25% charged
t-butyl acrylate/2-ethylhexyl methacrylate/polydimethylsiloxane molecular weight about 15,000.

Hydrophobic Volatile Solvent

The rinse-off hair care products of the present invention also comprise a hydrophobic volatile solvent. By "volatile" it is meant that the useful solvents have a boiling point less than about 225°C at 760 mm Hg. The hydrophobic, volatile solvent is insoluble in aqueous carriers of the composition. This is determined in the absence of the copolymer, or other emulsifying agents, and can easily be verified by observing whether the solvent and aqueous carrier form separate phases after being mixed at room temperature, as viewed without magnification.

The solvents useful in the present invention generally include hydrophobic, volatile branched hydrocarbons, silicone derivatives, preferably siloxanes, and mixtures thereof. Preferred hydrophobic, volatile branched chain hydrocarbons useful as the solvent herein contain from about 7 to about 14, more preferably from about 10 to about 13, most preferably from about 11 to about 12 carbon atoms. Saturated hydrocarbons are preferred, although it is not intended to exclude unsaturated hydrocarbons.

Representative examples of hydrophobic volatile hydrocarbon are Isopar® H and Isopar K® (C₁₁-C₁₂ isoparaffins). Isopar L® (C₁₁-C₁₃ isoparaffins), Isopar E® (C₈-C₉ isoparaffins) and isododecane.

Preferred silicones useful as the volatile hydrophobic solvent herein include volatile siloxanes such as phenyl pentamethyl disiloxane, phenylethylpentamethyl disiloxane, hexamethyl disiloxane, methoxy propylheptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, and mixtures thereof. Preferred among the silicones are cyclomethicones, examples of which include octamethyl cyclo tetrasiloxane and decamethyl cyclopentasiloxane, which are commonly referred to D4 and D5 cyclomethicone, respectively.

Carrier

The rinse-off hair care compositions of the present invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from about 30.0% to about 99.75%, preferably from about 70% to about 96%, most preferably from about 82% to about 92%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin.

Hair Conditioners

Where the hair care compositions are conditioner compositions, the carrier may comprise gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The gel vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification

1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0%, preferably 0.1% to about 5%, of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0%, preferably 0.1% to about 3%, of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as xanthan gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride). These vehicles are described in detail in U.S. Patent Number 5,100,658, issued to Bolich, R.E., et al. on March 31, 1992; U.S. Patent Number 5,104,646, issued to Bolich, R.E., et al. on April 14, 1992; U.S. Patent Number 5,106,609, issued to Bolich, R.E., et al. on April 21, 1992, all incorporated herein by reference.

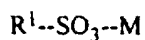
Shampoos

Where the hair care compositions are shampoo compositions, the carrier may include a surfactant material. The surfactant materials for the shampoo carriers of the invention comprise from about 5% to about 50%, preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with about 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to about 20% by weight C_{12-13} compounds; from about 60 to about 100% by weight of $C_{14-15-16}$ compounds, from about 0 to about 20% by weight of $C_{17-18-19}$ compounds; from about 3 to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to about 90% by weight of compounds having a degree of ethoxylation of from about 1 to about 4; from about 10 to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1 to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein R^1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid

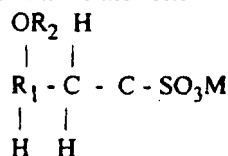
reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO₂, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO₂, etc., when used in the gaseous form.

The α-olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific α-olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, Pflaumer and Kessler, issued July 25, 1967, incorporated herein by reference.

Another class of anionic organic surfactants are the β-alkyloxy alkane sulfonates. These compounds have the following formula:



where R₁ is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R₂ is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as herein described.

Specific examples of β-alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium-β-methoxydecane-sulfonate, sodium 2-methoxy-tridecane-sulfonate, potassium 2-ethoxytetradecyl-sulfonate, sodium 2-isopropoxyhexadecyl-sulfonate, lithium 2-t-butoxytetradecyl-sulfonate, sodium β-methoxyoctadecyl-sulfonate, and ammonium β-n-propoxydodecyl-sulfonate.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

Rinse-off Compositions in General

Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene

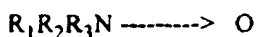
oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyldodecylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyldimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



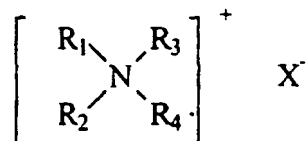
wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon

atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cerylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-triaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

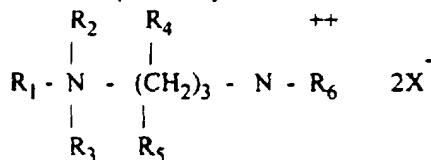
Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1 - R_4 are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and

alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

Other quaternary ammonium salts useful herein have the formula:

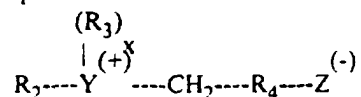


wherein R₁ is an aliphatic group having from about 16 to about 22 carbon atoms, R₂, R₃, R₄, R₅, and R₆ are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and X is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and ceryl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R₂ contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R₃ is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R₄ is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecyloxy]phosphonio]-2-hydroxy-propane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the RCONH(CH₂)₃ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof are preferred for use herein.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and copolymer plasticizing agents, such as glycerin and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

Plasticizers

Plasticization of the silicone grafted adhesive hair styling copolymers of the present invention can dramatically hinder the removability of the copolymers with normal shampooing. Without being limited by theory, it is believed that plasticization of the copolymer softens the polymer film on the hair, thereby decreasing the cohesive breaking stress and increasing the cohesive breaking strain of the polymer. This in turn results in the fracturing of the polymer film during shampooing rather than breaking of the adhesive bond to the hair. This results in incomplete removal of the copolymer and an eventual build-up of residue on the hair.

The compositions of the present invention are limited in the amount of materials which act as copolymer plasticizers. In preferred embodiments, the compositions of the present invention should be substantially free of such plasticizing materials, i.e. they should contain less than about 2%, preferably less than about 1%, and more preferably less than about 0.5% of such plasticizer materials. Plasticizing materials are generally relatively non-volatile organic liquids compatible with the copolymer component. By "non-volatile" it is meant that the boiling point of the liquids is greater than or equal to about 260°C. A nonlimiting list of exemplary material which act as plasticizers of the copolymers of the present invention includes diisobutyl adipate, acetyl tri-n-butyl citrate, di(2-ethyl hexyl) azelate, 2-ethyl hexyl diphenyl phosphate, diisooctyl isophthalate, isooctyl benzyl phthalate, butyl stearate, tri-2-ethyl hexyl trimellitate, N-octyl neopentanoate, diisostearyl malate, colloidal fumed silica (such as Cab-O-Sil®, sold by Cabot Corp.) and most perfume materials. Formulation experimentation, is required to determine whether plasticizer levels in the formula impact the adhesive strength, cohesive breaking stress and cohesive breaking strain of the present invention.

pH

The pH of the present compositions should be between about 3 and about 9, preferably between about 4 and about 8.

Residue Index

The rinse-off hair care compositions of the present invention have a residue index on hair of about 20 or greater, preferably of about 35 or greater, and more preferably of about 50 or greater.

The residue index, on hair, of the compositions of the present invention, can be measured by various *in vitro* techniques. For example, a preferred method is one wherein the compositions are evaluated on human hair switches in repeated cycles comprising the steps of shampooing the hair switch with a surfactant solution, treating the hair switch with the rinse-off composition to be evaluated, rinsing the hair switch, and drying the hair switch. The hair switch is evaluated for the presence of residue after a defined number of cycles.

For example, for determining a residue index, it is found particularly useful to visually examine the hair switch for the presence of a visible residue after the completion of multiples of five treatment cycles, e.g. after 5, 10, 15, 20, 25, and 30 cycles, and so forth, until the desired visual end point is achieved. The residue index is defined herein as the number of treatment cycles, in 5 unit increments, after which a visible residue is first visually observed on the hair.

As mentioned above, the compositions of the present invention do not leave a visible residue on the hair switches, i.e. they do not exhibit a visible residue until after about 20 or more cycles. In other words, such compositions have a residue index of about 20 or greater. More preferred are compositions which do not exhibit a visible residue until after about 35 or more cycles, in other words such compositions have a residue index of about 35 or greater. Even more preferred are compositions which do not exhibit a visible

residue until after about 50 or more cycles, in other words such compositions have a residue index of about 50 or greater. Even though there is no upper limit on the residue index, it is recognized that the higher the index, the better the performance of the composition in not leaving a visible residue upon the hair.

In the present invention the preferred method for measuring the residue index is as follows:

The residue index measurements are made on switches of human hair that have been arranged in the shape of a ponytail, i.e the hair is firmly glued together at one end. Switches containing twenty grams of dark brown, fine, virgin hair having an overall length of about 8 inches are used herein. These switches contain hair fibers having an overall length of about 8 inches and an average hair fiber diameter of about 40 to about 70 microns. The average hair fiber diameter is determined by making measurements on at least 10 hair fibers in the switch sample. The hair fiber diameter can be verified using a micrometer or standard microscopic techniques familiar to one of ordinary skill in the art of cosmetic science. By "virgin hair" is meant that the hair has not been subjected to chemical treatments such as bleaching or perming. The hair switches can be examined by standard electron microscopic techniques to evaluate the quality of the hair, e.g. the condition of the hair cuticles can be examined.

It is found convenient to evaluate the residue index of a rinse-off composition on several hair switches. The hair switches are wetted under a water spray tap with a water temperature of 100°F and at a flow rate of 1 gallon per minute. It is preferable to use gloved hands (e.g. latex surgical gloves) when handling the hair to avoid contaminating the hair samples with skin oils and other materials. Using a syringe, 1 cc of a surfactant solution having the following percent weight percent composition is applied to the hair switch and worked into the hair for approximately 15 seconds.

Surfactant Solution For Residue Index Method

<u>Ingredient</u>	<u>Weight Percent</u>
Distilled Water	78%
Ammonium Laureth-3 Sulfate ¹	13%
Ammonium Lauryl Sulfate	9%

¹ Having an average of about 3 molecules of ethylene oxide incorporated per molecule (or alternatively, 3 moles of ethylene oxide per mole of surfactant).

The hair switch is next rinsed with water (100°F; 1 gallon/minute) for 15 seconds wherein the hair switch is gently squeezed three times while running the fingers along the length of the hair switch. The excess water is squeezed from the hair. Using a syringe, the switch is then treated with about 6 cc of the rinse-off composition to be evaluated which is worked into the hair for approximately 15 seconds. The hair switch is next rinsed with water (100°F, 1 gallon/minute) for 15 seconds wherein the hair switch is gently squeezed twelve times while running the fingers along the length of the hair switch. The excess water is

squeezed from the hair. The hair switch is next hung to dry in a chamber having an air temperature of about 100°F, in which the air flow is minized to avoid disturbing the switches, for about 60 minutes. These steps of surfactant washing, rinsing, treatment with the rinse-off composition, rinsing, and air-drying constitute one cycle. After five such cycles are completed, the hair switch is visually examined while ungloved fingers are run through the switch to determine whether there is any visible composition residue on the hair strands. The residue must be one that is encircling the hair fibers. The presence of such encircling residues can be verified using any magnification techniques available to one of ordianry skill in the art. If no visible encircling residue is observed, additional groups of five cylces of surfactant washing, rinsing, treatment with the rinse-off composition, rinsing, and air-drying are repeated until a visible encircling residue is observed.

Once it is established that an encircling residue is present. The hair switch is subjected to two vigorous washes with 1 cc of the surfactant solution described above, each followed by a 15 second rinsing (100°F water; 1 gallon/minute). If the residue reamins after these two additional surfactant washings, the rinse-off composition is defined as having a residue index corresponding to that number of cycles completed prior to the two additional surfactant washings. If no visible residue is observed, after the two additional surfactant washings, groups of five additional treatment cycles are performed on other hair switch substrates until a visible residue is observed.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

METHOD OF USE

The rinse-off hair care compositions of the present invention are used in conventional ways to provide the hair cleaning/conditioning/styling/hold benefits of the present invention. Such methods of use depend upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which is then rinsed from the hair, as in the case of shampoos and conditioner products). By "effective amount" is meant an amount sufficient to provide the hair cleaning/conditioning/styling/hold benefits desired considering the length and texture of the hair, and the type of product used. Typical amounts are generally from about 0.5G to about 50 g of product. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to and rinsed from the hair, the hair is dried and styled in the usual ways of the user.

EXAMPLES

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

Ingredients are identified by chemical or CTFA name.

The following synthetic procedure is exemplary of the methods useful for synthesizing the copolymers of the present invention.

EXAMPLE I

Synthesis of Poly(*t*-butyl acrylate)-graft-polydimethylsiloxane]

Place 75 parts of *t*-butyl acrylate and 25 parts of polydimethylsiloxane macromonomer (11,000 MW) (commercially available from 3M, St. Paul, MN) in a flask. Add sufficient ethyl acetate as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with an inert atmosphere, preferably nitrogen or argon. Add initiator, (2,2'-azobisisobutyronitrile) to a level appropriate for the desired molecular weight. Typically this is in the range of about 0.25% to about 1.0% by weight relative to the amount of monomer. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature. The polymer is purified by drying off the reaction solvent in an oven.

By varying the monomers used, the general procedures given above in Example 1, is used to prepare other monomers and copolymers of the present invention.

The following Table 1 defines nonlimiting examples of copolymers that can be used in the hair care compositions shown in Examples 2-10. Each of the Examples 2-10 is illustrated with a given copolymer, however, any of the other copolymers from Table 1, or any other copolymers of the present invention can be employed. In Table 1, the relative weight percentages of the monomers added to the reaction mix are given.

TABLE 1

The following table defines the silicone copolymers used in the examples.

Copolymer #1	75/25	tert-butyl acrylate / polysiloxane-containing C monomer S1 polymer molecular weight about 900,000
Copolymer #2	80/20	tert-butyl acrylate / polysiloxane-containing C monomer S2 polymer molecular weight about 900,000
Copolymer #3	70/30	tert-butyl styrene / polysiloxane-containing C monomer S3 polymer molecular weight about 300,000

Copolymer #4	67/3/30	tert-butyl acrylate / acrylic acid / polysiloxane-containing C monomer S1 polymer molecular weight about 700,000
Copolymer #5	65/35	tert-butyl acrylate / polysiloxane-containing C monomer S4 polymer molecular weight about 1,000,000
Copolymer #6	70/5/25	tert-butyl acrylate / 2-ethylhexyl methacrylate / polysiloxane-containing C monomer S2 polymer molecular weight about 700,000

Polysiloxane-containing C monomer S1 has a molecular weight of about 11,000. Polysiloxane-containing C monomer S2 has a molecular weight of about 15,000. Polysiloxane-containing C monomer S3 has a molecular weight of about 20,000. Polysiloxane-containing C monomer S4 has a molecular weight of about 30,000. All polysiloxane-containing C monomers are prepared in a manner similar to silicone grafted monomer exemplified in U.S. Patent 4,728,571, Clemens, issued March 1, 1988, incorporated by reference herein.

EXAMPLE 2

The following is a hair conditioner composition representative of the present invention.

Component	Weight %
Water	Q.S. to 100%
Hydrophobically Modified Hydroxyethylcellulose [1]	0.25 %
Stearalkonium Chloride	0.87 %
Cetyl Alcohol	1.85 %
Stearyl Alcohol	0.21 %
Stearamidopropyl Dimethylamine	0.50 %
CF1213® (Dimethicone Gum) [2]	2.33%
Methylchloroisothiazolinone Methylisothiazolinone	0.03 %
Perfume	0.33 %
Copolymer # 2	2.00 %
SS4230® (Trimethylsiloxysilicate) [2]	0.21 %
Cyclomethicone D4	11.30%

[1] Polysurf 67® supplied by Aqualon

[2] Commercially available from GE

This product is prepared by dissolving the copolymer #2 in Cyclomethicone D4 (solvent). The SS4230® fluid is added to this solution. The other components (except Kathon and perfume) are mixed in a separate vessel at a temperature high enough (80 C) to melt the solids. The polymer/solvent mixture and the dimethicone gum are added separately to the other components after those have been cooled to at least

45°C. Finally, Kathon and perfume are added, and the product cooled to ambient. This composition is useful for application to the hair to provide conditioning and styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 3

The following is a hair conditioner composition representative of the present invention.

Component	Weight %
Water	Q.S. to 100 %
Hydroxyethyl Cellulose	0.50 %
Hydrogenated Ditallowdimethyl Amonium Chloride (Quaternium 18)	0.85 %
Cetyl Alcohol	0.90 %
Stearyl Alcohol	0.81 %
Ceteareth-20	0.50 %
Stearamidopropyl Dimethylamine (Lexamine S13)	0.22 %
CF1213® (Dimethicone Gum) [1]	1.33%
Methylchloroisothiazolinone Methylisothiazolinone	0.03 %
Perfume	0.33 %
Copolymer # 6	2.50 %
Cyclomethicone D4/D5 Blend [90/10]	11.30%

[1] Commercially available from GE

This product is prepared by dissolving the copolymer #6 in Cyclomethicone D4/D5 blend (solvent). The other components (except Kathon and perfume) are mixed in a separate vessel at a temperature high enough (80°C)) to melt the solids. The polymer/solvent mixture and the dimethicone gum are added separately to the other components after those have been cooled to at least 45°C. Finally, Kathon and perfume are added, and the product is cooled to ambient. This composition is useful for application to the hair to provide conditioning and styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 4

The following is a hair shampoo composition representative of the present invention.

Component	Weight %
Water	Q.S. to 100 %
Ammonium Lauryl Sulfate	3.14 %
Ammonium Laureth Sulfate	13.56 %

Ceryl Alcohol	0.45 %
Stearyl Alcohol	0.19 %
Coco Monoethanol Amide	3.00 %
Ethylene Glycol Distearate	2.00 %
Tricetyl Methyl Ammonium Chloride	0.50 %
Methylchloroisothiazolinone Methylisothiazolinone	0.03 %
Perfume	0.20 %
Copolymer # 3	4.00 %
Isododecane	7.40 %

This product is prepared by dissolving the copolymer #3 in isododecane (solvent). The other components are mixed in a separate vessel at a temperature high enough to melt the solids. The polymer/solvent mixture is added to the other components after those have been cooled. This composition is useful for application to the hair to provide cleansing and styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 5

The following is a hair shampoo composition representative of the present invention.

Component	Weight %
Water	Q.S. to 100 %
Cocoamidopropyl Betaine	8.30 %
Ammonium Lauryl Sulfate	2.12 %
Ammonium Laureth Sulfate	6.35 %
Coco Monoethanol Amide	1.50 %
Hydroxypropyl Methocellulose (K15)	0.25 %
Ethylene Glycol Distearate	1.50 %
Tricetyl Methyl Ammonium Chloride	0.50 %
Methylchloroisothiazolinone Methylisothiazolinone	0.03 %
Perfume	0.20 %
Copolymer # 5	3.00 %
Isododecane	10.00 %

This product is prepared by dissolving the copolymer #5 in isododecane (solvent). The other components are mixed in a separate vessel at a temperature high enough to melt the solids. The polymer/solvent solution is added to the other components after those have been cooled. This composition is useful for application to the hair to provide cleansing and styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 6

The following is a rinse-off hair styling gel composition representative of the present invention.

Component	Weight %
<u>Polymer-Solvent Mix</u>	
Copolymer # 1	1.25 %
Isopar H® [1]	3.75 %
<u>Premix</u>	
Water	43.00 %
Hydrogenated Ditallowdimonium Chloride (Quaternium 18)	1.00 %
<u>Main Mix</u>	
Water	50.00 %
Carbopol 940®	0.75 %
Panthenol	0.05 %
Perfume	0.20 %

[1] C₁₁-C₁₂ Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dissolving the copolymer #1 in Isopar H®. Quaternium 18 is mixed with water at 80°C. The polymer-solvent mixture is added to the Quaternium 18 containing premix at either high or low temperature. The other components are mixed in a separate vessel at ambient temperature. The Quaternium 18 premix with the polymer/solvent mixture is cooled (if needed) and added to the other components. This composition is useful for application to the hair to provide conditioning, styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 7

The following is a rinse-off hair spray-on gel composition representative of the present invention.

Component	Weight %
Water	Q.S. to 100 %
Tallowtrimonium Chloride	0.10 %
Hydrogenated Ditallowdimonium Chloride (Quaternium 18)	0.90 %
Panthenol	0.05 %
Perfume	0.20 %
Copolymer # 2	1.00 %
Hexamethyl disiloxane	3.00 %

This product is prepared by dissolving the copolymer #2 in hexamethyl disiloxane (solvent). The other components are mixed in a separate vessel at a temperature high enough (70 C) to melt the solids.

The polymer/solvent solution is added to the other components at either high or low temperature. This composition is useful for application to the hair to provide conditioning, styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 8

The following is a hair styling rinse composition representative of the present invention.

Component	Weight %
<u>Premix A</u>	
Water	4.98 %
Ditallowdimonium Chloride (Varisoft 470)	1.43 %
CF1213® (Dimethicone Gum) [2]	2.33%
Amodimethicone	0.10 %
<u>Premix B</u>	
Water	9.97 %
Stearalkonium Chloride	0.30 %
Panthenol DL	0.225 %
Pantyl Ethyl Ether	0.025 %
<u>Main Mix</u>	
Water	67.49 %
Hydrophobically Modified Hydroxyethylcellulose [1]	1.23 %
Xanthan Gum	0.25%
Citric Acid	0.02 %
Sodium Citrate	0.09 %
Cetyl Alcohol	0.12 %
Stearyl Alcohol	0.08 %
<u>Polymer-Solvent Mixture</u>	
Copolymer # 1	1.75 %
Cyclomethicone D4/D5 Blend [70/30]	8.54 %
SS4230® (Trimethylsiloxysilicate) [2]	0.21 %
Methylchloroisothiazolinone Methylisothiazolinone	0.03 %
Perfume	0.33 %
Benzyl Alcohol	0.50 %

[1] Polysurf 67® supplied by Aqualon

[2] Commercially available from GE

This product is prepared by dissolving the copolymer #1 in the cyclomethicone D4/D5 blend (solvent). The SS4236 is added to the polymer solution. Premixes A and B are prepared by combining materials at 70°C. Premix A goes through a colloid mill and is cooled to 38°C. Materials in 'Main Mix', except benzyl alcohol, are mixed at 65°C. The polymer solution is then added to the 'Main Mix'. Main mix goes through a colloid mill and is cooled to 38°C. Premixes and 'Main Mix' are combined at 38°C. Then the benzyl alcohol is added. This composition is useful for application to the hair to provide conditioning, styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 9

The following is a hair styling rinse composition representative of the present invention.

Component	Weight %
<u>Premix A</u>	
Water	4.67 %
Ditalowdimonium Chloride (Varisoft 470)	1.00 %
Dimethicone Gum (15% in Cyclomethicone D5) [2]	1.00 %
Amodimethicone	0.40 %
<u>Premix B</u>	
Water	9.36 %
Stearalkonium Chloride	0.15 %
Panthenol DL	0.225 %
Pantyl Ethyl Ether	0.025 %
<u>Main Mix</u>	
Water	63.53 %
Hydrophobically Modified Hydroxyethylcellulose [1]	1.00 %
Xanthan Gum	0.10%
Citric Acid	0.02 %
Sodium Citrate	0.09 %
Cetyl Alcohol	0.60 %
Stearyl Alcohol	0.40 %
<u>Polymer-Solvent Mixture</u>	
Copolymer # 4	2.50 %
Cyclomethicone D4/D5 Blend [95/5]	14.17 %
Methylchloroisothiazolinone Methylisothiazolinone	0.03 %
Perfume	0.33 %
Benzyl Alcohol	0.50 %

[1] Polysurf 67® supplied by Aqualon

[2] Commercially available from GE

This product is prepared by dissolving the copolymer #4 in the cyclomethicone D4/D5 blend (solvent). Premixes A and B are prepared by combining materials at 70°C. Premix A goes through a colloid mill and is cooled to 38°C. Materials in Main Mix, except benzyl alcohol, are mixed at 65°C. The polymer solution is added to the Main Mix. Main mix goes through a colloid mill and is cooled to 38°C. Premixes and Main Mix are combined at 38°C. Then the benzyl alcohol is added. This composition is useful for application to the hair to provide conditioning, styling and hold benefits. This composition has a residue index of about 20 or greater.

EXAMPLE 10

The following is a rinse-off hair styling mousse composition representative of the present invention.

Component	Weight %
Water	Q.S. to 100 %
Tallowtrimonium Chloride	0.10 %
Hydrogenated Ditallowdimonium Chloride (Quaternium 18)	0.90 %
Lauramine Oxide	0.20 %
Panthenol	0.05 %
Perfume	0.20 %
Copolymer # 2	1.00 %
Hexamethyl disiloxane	3.00 %
Isobutane	7.00 %

This product is prepared by dissolving the copolymer #2 in hexamethyl disiloxane (solvent). The other components (except isobutane) are mixed in a separate vessel at a temperature high enough (70°C) to melt the solids. The polymer/solvent solution is added to the other components after those have been cooled. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts Isobutane. This composition is useful for application to the hair to provide conditioning, styling and hold benefits. This composition has a residue index of about 20 or greater.

When the compositions defined in Examples II-X are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

WHAT IS CLAIMED IS:

1. A rinse-off hair care composition characterized in that it comprises:

A. from 0.25% to 70%, preferably from 4% to 30%, more preferably 8% to 18%, by weight of a copolymer component comprising:

i. from 1.5% to 70%, preferably 5% to 40%, more preferably 10% to 25%, by weight of said copolymer component, of a silicone-grafted adhesive hair styling copolymer having a weight average molecular weight from 300,000 to 5,000,000, preferably from 500,000 to 2,000,000, more preferably from 600,000 to 1,500,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising monomers selected from the group consisting of A monomers, B monomers, C monomers and mixtures thereof;

wherein the weight percent of said copolymer in said rinse-off hair care composition is from 0.10% to 7%, preferably from 1% to 4%, more preferably 1.5% to 2.5%; and

wherein said copolymer is prepared by the polymerization combination of the following relative weight percentages of said A monomers, said B monomers, and said C monomers:

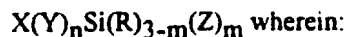
a. from 45% to 85%, preferably from 60% to 85%, more preferably from 70% to 80%, most preferably from 70% to 75% of a hydrophobic, vinyl A monomer, free radically copolymerizable with said B monomers and said C monomers;

b. from 0% to 5%, preferably from 0% to 3% of a hydrophilic, reinforcing B monomer, copolymerizable with said A monomer and said C monomer, said B monomer being selected from the group consisting of polar monomers and macromers and mixtures thereof; and

c. from 15% to 50%, preferably from 15% to 40%, more, preferably from 20% to 30% of a polysiloxane-containing C monomer, copolymerizable with said A monomer and said B monomer, having:

a weight average molecular weight of from 5,000 to 50,000, preferably from 5,000 to 30,000, more preferably from 8,000 to 25,000; and

having the general formula:



X is a vinyl group copolymerizable with said A monomers and said B monomers;

Y is a divalent linking group;

R is a hydrogen, lower alkyl, aryl or alkoxy;

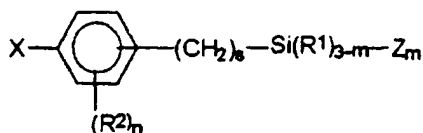
Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 1500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

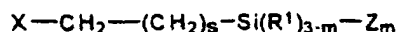
m is an integer from 1 to 3; and

- ii. from 30% to 98.5% by weight of said copolymer component, of a hydrophobic volatile solvent; and
 - B. from 30% to 99.75%, preferably from 70% to 96%, more preferably from 82% to 92%, of a carrier suitable for application to hair; and wherein said rinse-off hair care composition has a residue index on hair of greater than 20, preferably greater than 35 and more preferably greater than 50.
2. A rinse-off hair care composition according to Claim 1 wherein said silicone-grafted adhesive hair styling copolymer of the copolymer component is prepared by the polymerization combination of the following relative weight percentages of said A monomers, said B monomers, and said C monomers:
 - a. from 55% to 75% of said hydrophobic, vinyl A monomer;
 - b. from 0% to 5% of said hydrophilic, reinforcing B monomer; and
 - c. from 25% to 40%, preferably from 25% to 30% of said polysiloxane-containing C monomer wherein said C monomer has a weight average molecular weight of from 5,000 to 13,000, preferably from 8,000 to 13,000.
 3. A rinse-off hair care composition according to Claim 1 wherein said silicone-grafted adhesive hair styling copolymer of the copolymer component is prepared by the polymerization combination of the following relative weight percentages of said A monomer, said B monomers and said C monomers:
 - a. from 45% to 80% of said hydrophobic, vinyl A monomer;
 - b. from 0% to 5% of said hydrophilic, reinforcing B monomer; and
 - c. from 20% to 50%, preferably from 20% to 30% of said polysiloxane-containing C monomer, wherein said C monomer has a weight average molecular weight of from 13,000 to 50,00, preferably from 13,000 to 25,000.
 4. A rinse-off hair care composition according to any of Claims 1 to 3, wherein said hydrophobic, vinyl A monomer is selected from the group consisting of acrylic acid esters, methacrylic acid esters, vinyl compounds, vinylidene compounds, unsaturated hydrocarbons, C₁-C₁₈ alcohol esters of organic acids and organic acid anhydrides, and mixtures thereof, and is preferably selected from the group consisting of t-butyl acrylate, t-butyl methacrylate, t-butyl styrene, and mixtures thereof.

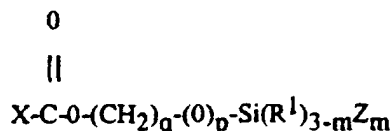
5. A rinse-off hair care composition according to any of Claims 1 to 4, wherein said hydrophilic, reinforcing B monomer is selected from the group consisting of unsaturated organic mono- and poly- carboxylic acids, unsaturated (meth)acrylates, unsaturated (meth)acrylamides, unsaturated (meth)acrylate alcohols, unsaturated aminoalkylacrylates, unsaturated organic acid anhydrides, unsaturated esters of organic acid anhydrides, hydrophilic unsaturated vinyl compounds, hydrophilic unsaturated allyl compounds, hydrophilic unsaturated imides, salts of the foregoing compounds, and mixtures thereof; and is preferably selected from the group consisting of acrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, t-butyl acrylamide, vinyl pyrrolidone, salts of acids and amines listed above, and mixtures thereof.
6. A rinse-off hair care composition according to any of Claims 1 to 5, wherein said polysiloxane-containing C monomer has a formula selected from the following group:



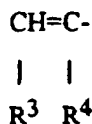
or



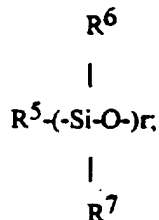
or



wherein s is 0, 1, 2, 3, 4, 5 or 6; m is 1, 2 or 3, preferably 1; p is 0; q is 2, 3, 4, 5 or 6, preferably 3; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl, preferably methyl; R² is C1-C6 alkyl or C7-C10 alkylaryl; n is 0, 1, 2, 3 or 4; X is



wherein R³ is hydrogen or -COOH, preferably hydrogen; R⁴ is hydrogen, methyl or -CH₂COOH, preferably methyl; Z is



- R^5 , R^6 , and R^7 independently are lower alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen or hydroxyl, preferably all methyl; and r is an integer of from 100 to 350.
7. A rinse off hair care composition according to any of Claims 1 to 6, wherein said hydrophilic volatile solvent is selected from the group consisting of hydrophobic, volatile C_7 - C_{14} branched hydrocarbons, hydrophobic, volatile silicones and mixtures thereof, preferably is selected from the group consisting of isododecane, cyclomethicone and mixtures thereof.
 8. A rinse-off hair care composition according to any of Claims 1 to 7, wherein said carrier comprises a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, preferably selected from the group consisting of alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.
 9. A rinse-off hair care composition according to any of Claims 1 to 7, wherein said carrier comprises a conditioner which further comprises:
 - A. from 0.1% to 10% of a lipid vehicle material, preferably selected from the group consisting of cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and
 - B. from 0.05% to 5% of a cationic surfactant, preferably a quaternary ammonium surfactant.
 10. A method for delivering both hair conditioning and hair style retention to human hair by administering a safe and effective amount of the composition of any of Claims 1 to 9, to a human in need of such treatment.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06 A61K7/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 92 16179 A (PROCTER & GAMBLE) 1 October 1992 see page 5, line 16 - page 6, line 15; claims 1-10; examples VIII-IX ---	1-10
X	WO 93 23446 A (PROCTER & GAMBLE) 25 November 1993 see claims 1-12; examples IX-X ---	1-10
X	WO 95 04518 A (PROCTER & GAMBLE) 16 February 1995 see claims 1-10; examples 1-10 ---	1-10
X	WO 95 05800 A (PROCTER & GAMBLE) 2 March 1995 see claims 1-10; examples I-III, V, X -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9216179 A	01-10-92	AU 1677292 A	21-10-92
		BR 9205788 A	07-06-94
		CA 2104858 A	20-09-92
		CN 1066383 A	25-11-92
		CZ 9301945 A	16-03-94
		EP 0576598 A	05-01-94
		HU 66183 A	28-10-94
		JP 6506219 T	14-07-94
		NO 933283 A	18-11-93
		NZ 242024 A	26-07-95
		SK 100593 A	06-07-94
		TR 26384 A	15-03-95
WO 9323446 A	25-11-93	AU 677005 B	10-04-97
		AU 4243393 A	13-12-93
		CA 2135186 A	25-11-93
		CN 1081195 A	26-01-94
		CZ 9402773 A	16-08-95
		EP 0640105 A	01-03-95
		FI 945358 A	14-11-94
		HU 70074 A	28-09-95
		JP 7508060 T	07-09-95
		NO 944303 A	13-01-95
		SK 136194 A	09-08-95
WO 9504518 A	16-02-95	AU 7336694 A	28-02-95
		BR 9407180 A	17-09-96
		CA 2167483 A	16-02-95
		CN 1132473 A	02-10-96
		CZ 9600338 A	17-07-96
		EP 0712309 A	22-05-96
		FI 960494 A	02-04-96
		HU 73652 A	30-09-96
		JP 9501428 T	10-02-97
		NO 960451 A	02-04-96
		US 5565193 A	15-10-96
WO 9505800 A	02-03-95	AU 7602294 A	21-03-95
		BR 9407633 A	28-01-97
		CA 2168876 A	02-03-95

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9505800 A		CN 1133557 A	16-10-96
		EP 0714285 A	05-06-96
		JP 9501934 T	25-02-97
		US 5567428 A	22-10-96
